CHAPTER 1

INTRODUCTION

There are two problems with using fossil fuel. First, they are limited in amount and sooner or later will be depleted. The second is that fossil fuels are causing serious environmental problems (Barbir, 2005). Early in the 1970s hydrogen energy system had been proposed as a solution of these global problems. Hydrogen can be converted to electricity in fuel cells with higher efficiencies than conversion of fossil fuel to mechanical energy in internal combustion engines or to electrical energy in thermal power plants. However, fuel cell and its components are still on development.

1.1 Fuel cell and bipolar plate

A fuel cell is an energy conversion device. It is an electrochemical device that converts chemical energy of fuel and oxidant into electricity directly. Fuel cell are not exhaustible like batteries and unlike internal combustion engines, they do no burn fuel and therefore do not generate pollutants.

Research has been conducted and is currently being conducted into several types of fuel cells. Proton exchange membrane (PEM) fuel cells represent a particular class having desirable properties. They operate at relatively low temperature (70-90 ˚C), smaller in volume and lighter in weight than other fuel cells. PEM fuel cell use hydrogen and oxygen as fuel and oxidant respectively.

A single PEM fuel cell is comprised of three types of components: a membrane-electrode assembly (MEA), two seals and two current collectors. In its simplest form, the MEA consists of a membrane, two dispersed catalyst layers, and two gas diffusion layers (GDL) (Mehta and Cooper, 2003). The membrane separates the half reactions allowing protons to pass through to complete the overall reaction. The electrons created on the anode side are forced to flow through an external circuit there by creating electrical current. Pressed against the outer surface of each GDL is a piece of hardware called the bipolar plate (or polar plate in case of individual single cell) that typically serves as both gas flow field and current collector. A single cell can only give an output voltage around 0.5-0.7 volt. The cells can be stacked together in series by the bipolar plates to achieve higher total voltage. In a fuel cell stack, each bipolar plate supports two adjacent cells. They have been used to distribute the fuel and oxidant within the cell, separate the individual cells, carry current away from each cell, carry water, humid gases and keep the cell cool.

Traditionally, carbon-based materials have been used as bipolar plate, because of their chemical stability in a fuel cell environment and because they produce the highest electrochemical power output. However, the lack of mechanical strength of carbon-based material limits the size and hence the volumetric power density (Hodgson et al., 2001; Hermann et al., 2005). Other materials are being evaluated with the aim of producing low voltage drop and long lifetime. The alternatives to graphite fall into composite materials and metal. Metallic bipolar plates (Wind et al., 2002; Lee et al., 2003; 2004; 2005; Silva et al., 2006; Jayaraj et al., 2005; Wang et al., 2003; 2004) offer the potential for mechanical strength, gas permeability, reduced weight/volume, at significantly lower cost. Stainless steel is a low-cost material that is easy to shape, and thin sheets can be used to yield low volume and weight (Makkus et al., 2000)

In PEM fuel cell, bipolar plates are exposed to an operating environment with a pH of 2-3. If it does not be properly designed, dissolution or corrosion of the metal is occurrence. When the metal plate is dissolved, the dissolved metal ions diffuse into the membrane and are trapped at ion exchange cites, resulting in a lowering of ionic conductivity. In addition, a corrosion layer on the surface of a bipolar plate increases the electrical resistance and decreases the output of the cell (Mehta and Cooper, 2003). Because of these issues, metallic bipolar plates are designed with a protective coating layer. The coating for bipolar plates should be conductive and non-corrosive to protect the substrate from the operating environment.

1.2 Metallic bipolar plate coating

In the following some concepts of conductive and protecting coated are considered. Conducting oxide and plasma treatments can be delivered by low-cost processes suitable for this and other applications. Zinc oxide (ZnO) and Al-doped zinc oxide (ZnO:Al) have been developed for a number of applications (Jeong et al., 2006) other than fuel cells but could be of great value to fuel cells. Metal nitrides and metal carbides are not only hard but also of good electrical conductivity. Plasma nitriding and carburizing of austenitic stainless steel are widely used to improve the surface hardness and wear resistance (Liang et al., 2000; Sun, 2005), but also much improved corrosion resistance (Liang, 2003; Baranowska and Arndd, 2004; Lei and Zhu, 2001).

The purpose of this research is followed the DOE (Department of Energy, United States of America) technical target for bipolar plates on 2010. The DOE request for Interfacial Contact resistance (ICR) is lower than 10 $m\Omega.cm^2$ at compaction force of 150 N/cm^2, corrosion current simulated in PEM fuel cell environment <1 $\mu A/cm^2$ at -0.1 V with H_2 purge (anode side) and at 0.6 V with air purge (cathode side). The bipolar plates bulk electrical conductivity >100 S/cm with the weight of 0.4 kg/kW for fuel cell stack (DOE annual progress report, 2008). The fiscal year (FY) 2008 progress report of DOE hydrogen program on nitride metallic bipolar plates (Brady et al., 2008) had shown the results of a research group at ORNL (Oak Ridge National Laboratory) that thermally nitride of ferritic alloy had low ICR and excellent corrosion resistance in aggressive PEM fuel cell environments. In addition, this group of researchers also has continues to characterize conductive oxides as coating. For fuel cell application, the optical transparency is of no importance. We can focus on optimizing these materials for high conductivity and corrosion resistance.

Zinc oxide (ZnO) is a well-known semiconductor. The researchers are very interested in zinc oxide thin film because of their applications in many devices. Among the different deposition methods, magnetron sputtering is mostly used (Yang et al.,1998; Tominaga et al.,2001; Herrmann et al., 2003; Jayaraj et al., 2002; Hong et al., 2003a; Hong et al., 2003b). The microstructure and electrical properties of the films can be controlled by deposition parameters (Tzolov et al., 2001), such as gas pressure, substrate position and doped impurity concentration in sputtering target (Tominaga et al., 2001). Highly conductive ZnO films can be prepared by doping with a few atomic percent of aluminum. The lowest resistivity obtained at the Al-doped about 5-7 atomic percent (Lee et al., 2004; Ruth et al.,1989). Al-doped zinc oxide (ZnO:Al) films also have a high temperature stability (Hong et al.,2003). The electrical resistivity of ZnO and ZnO:Al films can be obtained lower than $5\text{x}10^{-4}$ Ω cm depend on deposition conditions (Hong et al., 2003a; Hong et al., 2003b). The minimum resistivity obtained at the oxygen pressure of 25 mPa and substrate temperature 150 ˚C. In this region, the films possess high carrier concentration and Hall mobility (Hong et al., 2003a). Some articles also shown that the lowest resistivity of ZnO:Al film was achieved at a bias voltage of approximately -60 volt (Ma et al., 2002). Zinc oxide is presently of interest due to its potential use as conducting oxide. In addition, zinc treatment of metal substrate can protect against corrosion too (Ziemniak and Hanson, 2006; Arenas et al., 2005; Martins et al., 2004).

One of the widely used techniques for improving surface hardness, wear resistance and other properties of ferrous and non-ferrous materials are plasma nitriding and plasma carburizing (Liang et al., 2000; Larisch et al., 1999; Borgioli et al., 2006; Yin, 2005; Farrell et al., 2005; Ismail, 1981; Fossati et al., 2000). With plasma assisted nitride and carburize technique, a layer of compound is produced at the surface of austenite stainless steel. This layer has high hardness and good corrosion resistance (Liang et al., 2000; Mändl et al., 2005; Tian et al., 2002). The stainless steel can be treated with N_2 and other hydrocarbon gas under the temperature below 450 ˚C. The working pressure around 0.3-0.4 Pa and negative voltage apply to the sample are about 1 kV can produce nitride layer (Liang et al., 2000).

Transition metal nitrides and carbides are of interest for a wide variety of functional coating application due to their unique combination of properties. Such as high hardness, good electrical conductivity, chemical stability, etc. (Brady et al., 2004). For the bipolar plate application, one should distinguish between the bulk and total conductivity or resistivity. In an actual fuel cell stack, interfacial contact resistance (ICR) is more important than bulk resistance (Barbir, 2005 : 103). Several articles have shown that interfacial contact resistance of nitride stainless steel and carbon papers have very low interface contact resistance. Wang et al. (2004) found that the best ICR was around 40 mΩ cm^2 at a compaction force of 150 N cm^{-2}. They had the corrosion test of thermally nitride stainless steel by potentiostatic polarization measurements in simulated PEM fuel cell environments has shown that; in the cathodic side, the corrosion current density quickly stabilized to about 0.6x10^{-6} A cm^{-2} and the corrosion current density stabilized on the order of -1x10^{-6} A cm^{-2} under the simulated anodic condition.

1.3 Overview of Thesis

According to the purpose of this research on the coating of metallic bipolar plates for conductive and non-corrosive, the subjects have dealings with fuel cell bipolar plate, coating technique and characterization. Thus, this research begins with a review of fuel cell basic, principles of plasma coating and analysis principles in Chapter 2.

Next chapter, chapter 3, we will explain about the experimental details. Several coating was produce by different technique. There are three techniques used in this research; Filtered Cathodic Vacuum Arc (FCVA), reactive magnetron sputtering and plasma immersion. All techniques are required to produce non-corrosive and conductive coating. The experimental procedure and films properties analysis will be discussed in this chapter.

In chapter 4, we talk about the experimental results and discussions. The results of thin films produced by FCVA will be showed for electrical properties and microstructure. The other films with other coating technique are showed with its electrical properties and corrosion resistance. The fuel cell polarization curve with treated AISI 304 bipolar plate will show in the end of this chapter.

The last chapter is devoted to the conclusions. There are two parts in this chapter. First, we concern with the films produced by FCVA technique which is not applied for bipolar plate. The other part, we conclude the results of treated AISI 304 bipolar plate application in PEM fuel cell.